Cyclophanes as Model Compounds for Permanent, Dynamic Aggregates – Induced Chirality with Strong CD Effects

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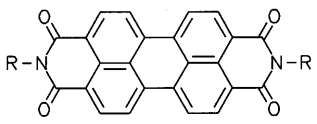
Dynamic processes, a bathochromically shifted fluorescence, and strong solvent-induced chirality effects are observed for the [12,12]-perylene-bis(imide)-cyclophane **3**, which forms a "fixed supramolecule".

The spontaneous self-organization of organic compounds is a modern research topic of particular interest. Chromophores are good probes for the investigation of such effects because a self-organization corresponds to an aggregation and is accompanied by a characteristic alteration of the UV/Vis spectra. Unfortunately, the formation of aggregates cannot easily be controlled and is limited to certain concentration ranges. On the other hand, chromophores can be bound to give dimers in the form of cyclophanes, which persist even under high-dilution conditions (for novel work concerning cyclophanes, see refs.[1][2]). We have chosen perylene-3,4:9,10-bis(dicarboximides) **1** (perylene dyes; for a review, see ref.[3]) not only because of their chemical and photochemical persistency and high coefficients of extinction, but also because nodes[3][4] in their HOMOs and LUMOs occur at the nitrogen atoms, so that there is a "closed chromophore" at these centres, which renders the chromophore insensitive to substituent effects. We used a C-12 spacer for the cyclophane between the two chromophores in order to guarantee a sufficiently high solubility for the intended investigations, and therefore condensed 1,12-diaminocyclododecane with the bis(anhydride) **2**. A polymerization of the bifunctional components was prevented by employing the Ziegler-Ruggli dilution method, so that **3** was isolated in 27% yield after a reaction time of 2 weeks.



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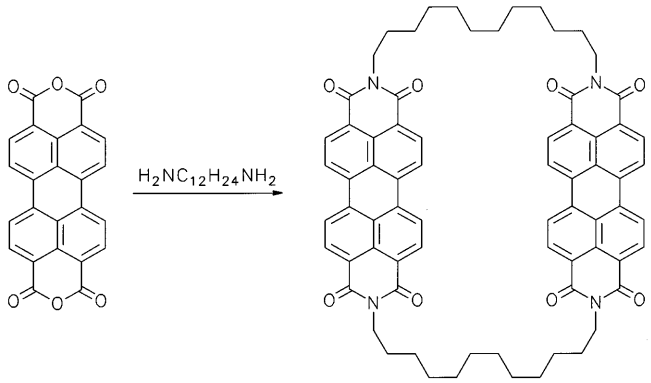
Cyclophane **3** is sufficiently soluble in chloroform to permit the recording of its UV/Vis spectrum, which exhibits a bathochromically shifted absorption (Figure 2). This is typical for an H-type stacking, where the chromophores are



2 **3**

layered on top of one another. This geometry is verified by the application of force-field[5] calculations and refinement by AM1 semiempirical quantum mechanical calculations[6][7][8]; see Figure 1.

The calculations indicate a rather high flexibility of **3** (reasonable energy minima were found, differing at most by 9 kcal/mol), which make it ideal for relaxation processes to lead to other conformations. Such a relaxation process is observed for the fluorescence of **3**, which is surprisingly bathochromically shifted compared to that of **1**. This bathochromic shift is typical for J-type stacking, where the chromophores are shifted or distorted with respect to one another. This can be explained in terms of a slipping from H to J stacking of the chromophores that occurs after the vertical optical excitation. The rather high fluorescence quantum yield for **3** of $\Phi = 40\%$ (see Experimental Section) gives a further proof of the J-type stacking, since an H-type stacking in the excited state would result in a loss of any fluorescence.[9]

The calculated structure of **3** is inherently chiral, as are the majority of other energetically attainable confor-

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Figure 1. Calculated structure of **3**; the distance between the chromophores is about 9 A and the *N,N,N,N* torsion angle is about 19°

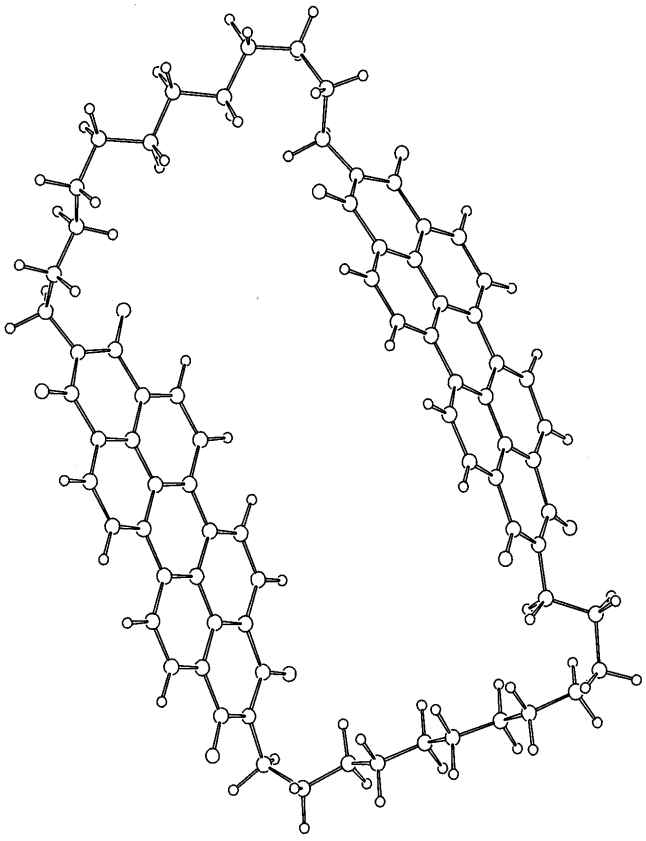
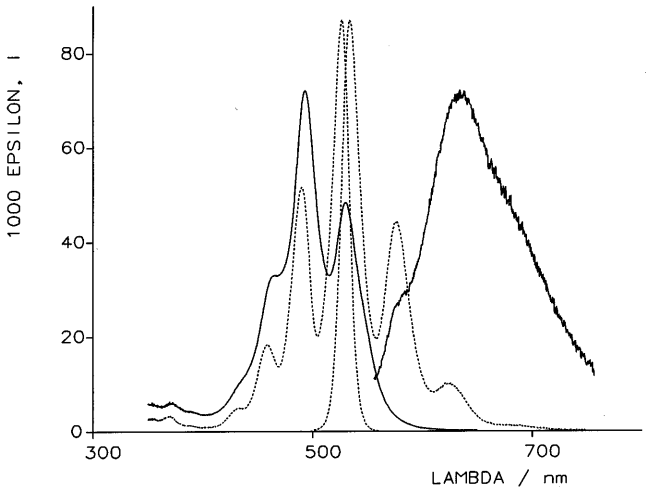
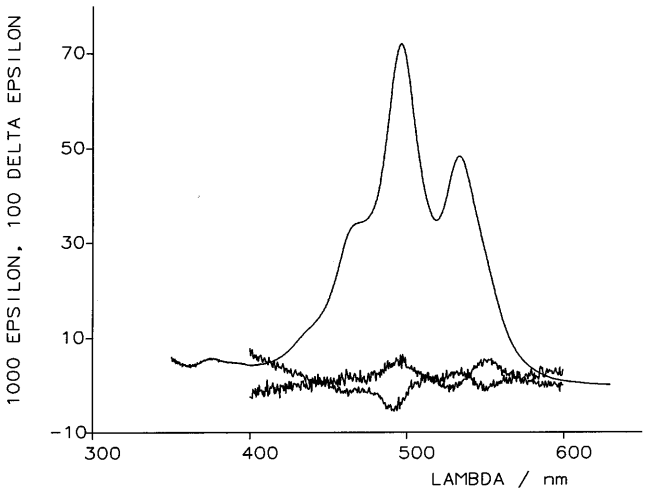


Figure 2. UV/Vis absorption and fluorescence spectra of **3** (—) (colour coordinates $x = 0.3986$, $y = 0.3193$, $Y = 63.71$, 2°, normlight C at $T_{min} = 0.1$) in chloroform compared to **1a** [R = $CH(C_6H_{13})_2$] (···).



mations. Of course, there is complete racemization in achiral solvents. We have tried to disturb the equal distribution by the application of the chiral solvent 1-phenylethylamine (compare, e.g. ref.[10]) and have observed the unusually high solvent-induced CD effects shown in Figure 3, i.e. a $\Delta\varepsilon$ of about 500 (monochromophoric perylene dyes such as **1a** exhibit only small CD effects in chiral, non-aggregated solvents[11]). These findings can be explained in terms of exciton effects[12][13] of **3**. (*S*)-(−)-Phenylethylamine induces a *P* chirality[14][15] of **3**, and (*R*)-(+)-phenylethylamine an *M* chirality. It is known that the transition moment of **1** is parallel to the molecular axis and therefore interesting insights in the induction of chirality by solvent effects can be obtained by the application of dyes such as **3**. This is also of importance for the synthesis of asymmetric compounds.

Figure 3. CD spectra of **3** in 1-phenylethylamine; at 500 nm, from top to bottom: absorption spectrum in (*S*)-(−)-phenylethylamine, CD spectrum in (*S*)-(−)-phenylethylamine, and CD spectrum in (*R*)-(+)-phenylethylamine ($E_{496} = 0.37$/1 cm)



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Experimental Section

N,N′-[12,12]-Perylene-3,4:9,10-bis(dicarboximide)-cyclophane (**3**): A hot suspension of 50 mg (0.12 mmol) of perylene-3,4:9,10-tetracarboxylic bis(anhydride) (**2**) in 50 ml of DMF and a hot solution of 1,12-diaminodocecane (0.26 mg, 0.12 mmol) in DMF (50 ml) were simultaneously added to refluxing DMF in a reflux dilution apparatus over a period of 2 weeks. The solvent was then removed in vacuo and the residue was treated with hot aqueous 10% K_2CO_3 and hot aqueous 2 N HCl, dried in air (16 h, 120°C), and then purified by column chromatography (silica gel; $CHCl_3$/ethanol, 10:1) to give 18 mg (27%) of **3** as a red-brown powder, m.p. > 320°C. − R_f (silica gel, chloroform/ethanol, 10:1) = 0.43. − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} s, 2929 m, 2855 m, 1697 s, 1658 s, 1595 s, 1579 w, 1508 w, 1441 m, 1404 m, 1382 w, 1344 m, 1257 w, 1170 w, 1094 w, 854 w, 811 m, 746 m. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 432.7 nm sh (5090), 466.0 (28100), 492.3 (65900), 529.3 (41900). − Fluorescence ($CHCl_3$): λ_{max} = 579 nm sh, 628, 681 sh. − Fluorescence quantum yield[16] [$E_{max} = 0.0144$ (492.3 nm, 1 cm) in $CHCl_3$, reference *N,N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 492 nm] = 40%. − CD [(*S*)-(−)-phenylethylamine, $E_{496} = 0.37$/1 cm]: $\lambda_{max}/\lambda_{min}$ ($\Delta\varepsilon$) = 552.0 nm (530), 529.2 (−86), 512.8 (160), 491.1 (−490). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.24 (m_c, 8 H, 4 CH_2), 1.4−1.6 (m, 24 H, 12 CH_2), 1.92 (m_c, 8 H, 4 CH_2), 4.16 (t, J = 7.8 Hz, 8 H, 4 CH_2), 7.91 (d, J = 7.8 Hz, 8 H, perylene), 8.24 (d, J = 7.8 Hz, 8 H, perylene). − MS (70 eV); *m/z* (%): 1115 (9), 1114 (31), 1113 (80), 1112 (100) [M^+], 1111 (2), 557 (2), 474 (2), 418 (2), 417 (3), 405 (4), 404 (7), 403 (6), 392 (6), 391 (16), 390 (6), 95 (2), 57 (2), 55 (3). − $C_{72}H_{64}N_4O_8$: calcd. 1112.4724; found 1112.4788 (MS). −

$C_{72}H_{64}N_4O_8$ (1112.5): calcd. C 77.66, H 5.80, N 5.03; found C 75.64, H 6.07, N 5.05.

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